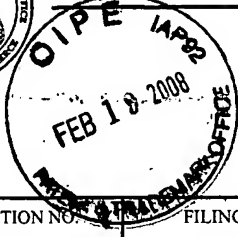




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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/802,087	03/16/2004	Ching-Yu Chang	2003-1435 / 24061.911	4048

42717 7590 02/04/2008
HAYNES AND BOONE, LLP
901 Main Street
Suite 3100
Dallas, TX 75202

EXAMINER

EL ARINI, ZEINAB

ART UNIT PAPER NUMBER

1792

MAIL DATE DELIVERY MODE

02/04/2008

PAPER

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Office Action Summary	Application No.	Applicant(s)	
	10/802,087	CHANG ET AL.	
	Examiner	Art Unit	
	Zeinab E. EL-Arini	1792	

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

- 1) ☒ Responsive to communication(s) filed on 04 December 2007.
- 2a) ☐ This action is **FINAL**. 2b) ☒ This action is non-final.
- 3) ☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

- 4) ☒ Claim(s) 1-27 is/are pending in the application.
- 4a) Of the above claim(s) _____ is/are withdrawn from consideration.
- 5) ☐ Claim(s) _____ is/are allowed.
- 6) ☒ Claim(s) 1-27 is/are rejected.
- 7) ☐ Claim(s) _____ is/are objected to.
- 8) ☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

- 9) ☐ The specification is objected to by the Examiner.
- 10) ☐ The drawing(s) filed on _____ is/are: a) ☐ accepted or b) ☐ objected to by the Examiner.
 Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).
 Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).
- 11) ☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

- 12) ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
- a) ☐ All b) ☐ Some * c) ☐ None of:
1. ☐ Certified copies of the priority documents have been received.
2. ☐ Certified copies of the priority documents have been received in Application No. _____.
3. ☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

- | | |
|--|---|
| 1) <input checked="" type="checkbox"/> Notice of References Cited (PTO-892) | 4) <input type="checkbox"/> Interview Summary (PTO-413) |
| 2) <input type="checkbox"/> Notice of Draftsperson's Patent Drawing Review (PTO-948) | Paper No(s)/Mail Date. _____ |
| 3) <input type="checkbox"/> Information Disclosure Statement(s) (PTO/SB/08) | 5) <input type="checkbox"/> Notice of Informal Patent Application |
| Paper No(s)/Mail Date _____ | 6) <input type="checkbox"/> Other: _____ |

Art Unit: 1792

DETAILED ACTION

1. Applicant's request for reconsideration of the finality of the rejection of the last Office action is persuasive and, therefore, the finality of that action is withdrawn.

Claim Rejections - 35 USC § 112

1. The following is a quotation of the second paragraph of 35 U.S.C. 112:

The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the applicant regards as his invention.

2. The rejection under 35 U.S.C. 112, second paragraph, stated in paper No.

20071112 has been withdrawn in view of applicants' remarks.

Double Patenting

3. The nonstatutory double patenting rejection is based on a judicially created doctrine grounded in public policy (a policy reflected in the statute) so as to prevent the unjustified or improper timewise extension of the "right to exclude" granted by a patent and to prevent possible harassment by multiple assignees. A nonstatutory obviousness-type double patenting rejection is appropriate where the conflicting claims are not identical, but at least one examined application claim is not patentably distinct from the reference claim(s) because the examined application claim is either anticipated by, or would have been obvious over, the reference claim(s). See, e.g., *In re Berg*, 140 F.3d 1428, 46 USPQ2d 1226 (Fed. Cir. 1998); *In re Goodman*, 11 F.3d 1046, 29 USPQ2d 2010 (Fed. Cir. 1993); *In re Longi*, 759 F.2d 887, 225 USPQ 645 (Fed. Cir. 1985); *In re Van Ornum*, 686 F.2d 937, 214 USPQ 761 (CCPA 1982); *In re Vogel*, 422 F.2d 438, 164 USPQ 619 (CCPA 1970); and *In re Thorington*, 418 F.2d 528, 163 USPQ 644 (CCPA 1969).

A timely filed terminal disclaimer in compliance with 37 CFR 1.321(c) or 1.321(d) may be used to overcome an actual or provisional rejection based on a nonstatutory double patenting ground provided the conflicting application or patent either is shown to be commonly owned with this application, or claims an invention made as a result of activities undertaken within the scope of a joint research agreement.

Effective January 1, 1994, a registered attorney or agent of record may sign a terminal disclaimer. A terminal disclaimer signed by the assignee must fully comply with 37 CFR 3.73(b).

4. Claim 1 is provisionally rejected on the ground of nonstatutory obviousness-type double patenting as being unpatentable over claims 1 and 8 of copending Application

Art Unit: 1792

No. 11/251,330. Although the conflicting claims are not identical, they are not patentably distinct from each other because the process and system in both applications are functionally equivalent. This is also because claim 1 does not include any cleaning step, therefore it is obvious from claims 1 and 8 of the co-pending application, and the process in both applications is functionally equivalent

This is a provisional obviousness-type double patenting rejection because the conflicting claims have not in fact been patented.

5. Claims 1-3 are provisionally rejected on the ground of nonstatutory obviousness-type double patenting as being unpatentable over claims 1, 2, and 8 of copending Application No. 11/384,624. Although the conflicting claims are not identical, they are not patentably distinct from each other because the process as claimed in claims 1-3 is obvious from claims 1-2 and 8 of the co-pending application. This is also because claim 1 does not include any cleaning step, and the process in both applications is functionally equivalent. This is a provisional obviousness-type double patenting rejection because the conflicting claims have not in fact been patented.

Claim Rejections - 35 USC § 103

6. The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

(a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negated by the manner in which the invention was made.

Art Unit: 1792

7. Claims 1-27 are rejected under 35 U.S.C. 103(a) as being unpatentable over Hazelton et al. (2006/0023185) in combination with Amblard et al. (7,056,646) and JP 402204468 (JP'468) and Ho et al. (7,070,915) new references.

Re. claims 1-27, Hazelton et al. teach a system of cleaning a wafer in an ILS apparatus with a cleaning liquid which has an affinity for the material absorbed on the wafer, which can be dirt and water. See the abstract, paragraphs 27, 29, 31-38 and 40, 44-51. With respect to the system (claims 15-19), see Figs. 1 and 10.

Hazelton et al. do not teach the surfactant, and means for providing surfactant, and the second fluid comprises NH_4OH , and H_2O_2 .

Amblard et al. disclose immersion lithography methods involving using a base developer as an immersion lithography fluid. See the abstract. The reference discloses that by employing a base developer as the immersion lithography fluid, the projection lens remains clean see col. 3, lines 2-6. Re. the immersed fluid containing surfactant, see col. 4, lines 25-29. The reference discloses that the fluid comprises solvents include de-ionized water, surfactants, and base compound comprises ammonium hydroxide. The reference discloses that it may be desirable to increase or decrease the index of refraction by making a slight increase or decrease in the concentration of the base compound in the immersion lithography fluid. See col. 4, lines 1-5.

Surfactants are known as a water-removing and drying agent, especially for removing water adhered on precise equipments, printed boards, and optical lenses, etc. See JP'468 (the abstract).

Ho et al disclose a method and system for drying a substrate. See the abstract, col. 3, lines 37-47, col. 4, lines 22-27, col. 5, line 10-col. 7, line 9.

It would have been obvious to one skilled in the art to replace the ethanol of Hazelton et al. with the surfactant of the Amblard et al. or JP'468, because both ethanol and surfactant have strong affinity to water. This is because Hazelton et al. disclose that any cleaning liquid may be used provided it has a sufficiently strong affinity to the liquid to be removed, see paragraph 35. Furthermore, since the means for applying the surfactant reads on any applicator in the ILS. Therefore, the claimed apparatus can be any typical ILS, as surfactant application is an intended use, see Ho et al. col. 5, lines 35-38, and the document in general. Re. claims 24, and 26-27, it is well known in the art to use H_2O_2 , and ozone in cleaning optical element.

Claim Rejections - 35 USC § 102

8. The following is a quotation of the appropriate paragraphs of 35 U.S.C. 102 that form the basis for the rejections under this section made in this Office action:

A person shall be entitled to a patent unless –

(e) the invention was described in (1) an application for patent, published under section 122(b), by another filed in the United States before the invention by the applicant for patent or (2) a patent granted on an application for patent by another filed in the United States before the invention by the applicant for patent, except that an international application filed under the treaty defined in section 351(a) shall have the effects for purposes of this subsection of an application filed in the United States only if the international application designated the United States and was published under Article 21(2) of such treaty in the English language.

9. Claims 1-5, and 8 are rejected under 35 U.S.C. 102(e) as being anticipated by Amblard et al (7,056,646).

Amblard et al. disclose a method for cleaning lens used in an immersion lithography system as claimed. See the abstract, col. 3, lines 2-16, and col. 4, lines 25-30.

Response to Arguments

10. Applicants' arguments with respect to claims 1-27 are unpersuasive. With respect to Hazelton et al. is not prior art, because the filing date of Hazelton is after March 16, 2004 filing date of the present application. Applicants' argument is unpersuasive, because the priority date for Hazelton et al. is April 11, 2003 and June 27, 2003. See 60/462,556 (pages 1-2), and 11/237,651 (2006/0023185) which is a continuation of PCT/US 2004/010309), see paragraphs 3-4, 9-10, and 34-35. See also a copy of PCT/US 2004/010309, page 2, line 13-30, page 4, line 20- page 5, line 3, page 5, line 28-page 6, line 2, and page 6, lines 8-31, and the document in general.

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11. With respect to the nonanalogous art, applicants' argument is persuasive; therefore Van Slyke reference has been withdrawn. With respect to the rejection under 35 U.S.C. 112, second paragraph, applicants' argument is persuasive; therefore the 112 rejection has been withdrawn. With respect to the double patenting rejections, applicants, argument is unpersuasive; therefore the double patenting rejections are maintained.

Conclusion

12. Applicant's arguments with respect to claims 1-27 have been considered but are moot in view of the new ground(s) of rejection.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Zeinab E. EL-Arini whose telephone number is 571-272-1301. The examiner can normally be reached on Monday.-Friday.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Michael Barr can be reached on 571-272-1414. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

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Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see <http://pair-direct.uspto.gov>. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

Zeinab E EL-Arini
Primary Examiner
Art Unit 1792

ZEE
/Zeinab E EL-Arini/
Primary Examiner, Art Unit 1792
1/30/08

Notice of References Cited	Application/Control No. 10/802,087	Applicant(s)/Patent Under Reexamination CHANG ET AL.	
	Examiner Zeinab E. EL-Arini	Art Unit 1792	Page 1 of 1

U.S. PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	Classification
*	A	US-7,056,646	06-2006	Amblard et al.	430/311
*	B	US-7,070,915	07-2006	Ho et al.	430/322
	C	US-			
	D	US-			
	E	US-			
	F	US-			
	G	US-			
	H	US-			
	I	US-			
	J	US-			
	K	US-			
	L	US-			
	M	US-			

FOREIGN PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Country	Name	Classification
	N	JP 02204468	08-1990	Japan		
	O					
	P					
	Q					
	R					
	S					
	T					

NON-PATENT DOCUMENTS

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
	U	PCT/US04/10309
	V	
	W	
	X	

*A copy of this reference is not being furnished with this Office action. (See MPEP § 707.05(a).)
Dates in MM-YYYY format are publication dates. Classifications may be US or foreign.

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First Hit Previous Doc Next Doc Go to Doc#

☐

L8: Entry 3 of 6

File: JPAB

Aug 14, 1990

PUB-NO: JP402204468A

DOCUMENT-IDENTIFIER: JP 02204468 A

TITLE: FLUORINATED HYDROCARBON MIXED SOLVENT COMPOSITION

PUBN-DATE: August 14, 1990

INVENTOR-INFORMATION:

NAME

COUNTRY

ASANO, AKIO

WATANABE, NAOHIRO

SAMEJIMA, SHUNICHI

KITAMURA, TATEO

KAMIMURA, TORU

ASSIGNEE-INFORMATION:

NAME

COUNTRY

ASAHI GLASS CO LTD

APPL-NO: JP01023939

APPL-DATE: February 3, 1989

US-CL-CURRENT: 510/285

INT-CL (IPC): C07C 19/08; C09K 3/00; C09K 3/30; C09K 5/00; C11D 7/50

ABSTRACT:

PURPOSE: To provide the subject composition having non-combustibility, etc., capable of reducing the using amounts of conventional chlorofluorocarbon(CFC) having an adhered water removing effect and suitable as an alternate fleon by comprising at least one of 1-chloro-1,1,2,2,3-pentafluoropropane, etc., and a surfactant.

CONSTITUTION: A composition comprises at least one selected from compounds of formulas I, II, III, IV, V, VI, VII, VIII, etc., and a surfactant such as preferably a polyoxyethylenepolyoxypropylene alkyl ether or caprylic acid caprylamine. The mixing amount of the surfactant in the composition is 0.1-5wt.% and the composition has a better adhered water-removing action than those of conventional CFC solvents, is used as a water-removing and drying agent after water washing processes especially for removing water adhered on precise equipments, printed boards, optical lenses, etc., and does not affect composite parts comprising metals, plastics, etc.

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⑫ 公開特許公報(A)

平2-204468

⑮ Int. Cl.⁵

識別記号

庁内整理番号

⑬ 公開 平成2年(1990)8月14日

C 07 C 19/08
C 09 K 3/00
3/30
5/00
C 11 D 7/50

111

C

8619-4H
6779-4H
7106-4H
8930-4H
6779-4H

審査請求 未請求 請求項の数 1 (全4頁)

⑭ 発明の名称 弗素化炭化水素系混合溶剤組成物

⑯ 特 願 平1-23939

⑰ 出 願 平1(1989)2月3日

⑱ 発 明 者 浅 野 昭 雄 神奈川県横浜市神奈川区三枚町543
⑱ 発 明 者 渡 辺 直 洋 千葉県千葉市都賀の台1-26-2
⑱ 発 明 者 鮫 島 俊 一 東京都中野区中央2-49-15
⑱ 発 明 者 北 村 健 郎 神奈川県藤沢市鵠沼桜が岡2-7-24
⑱ 発 明 者 上 村 徹 千葉縣市原市五井5232-2
⑲ 出 願 人 旭硝子株式会社 東京都千代田区丸の内2丁目1番2号
⑳ 代 理 人 弁理士 内 田 明 外3名

明 細 書

1. 発明の名称

弗素化炭化水素系混合溶剤組成物

2. 特許請求の範囲

1、 $\text{CCl}_2\text{F}_2\text{CF}_2\text{CHCl}_2$ 、
 $\text{CCl}_2\text{FCF}_2\text{CHCl}_2\text{F}$ 、
 $\text{CF}_3\text{CF}_2\text{CHCl}_2$ 、 $\text{CCl}_2\text{F}_2\text{CF}_2\text{CHCl}_2\text{F}$ 、
 $\text{CCl}_2\text{F}_2\text{CF}_2\text{CH}_2\text{Cl}$ 、
 $\text{CHF}_2\text{CF}_2\text{CHCl}_2\text{F}$ 、 $\text{CH}_3\text{CF}_2\text{CCl}_2\text{F}$ 、
 $\text{CHF}_2\text{CF}_2\text{CH}_2\text{Cl}$ 、
 $\text{CH}_2\text{ClCF}_2\text{CH}_2\text{Cl}$ 、 $\text{CHCl}_2\text{CF}_2\text{CH}_3$ 、
 $\text{CH}_3\text{CF}_2\text{CH}_2\text{Cl}$ 、 $\text{CHF}_2\text{CF}_2\text{CCl}_2\text{F}$ 、
 $\text{CHCl}_2\text{FCF}_2\text{CHCl}_2\text{F}$ 、
 $\text{CHF}_2\text{CF}_2\text{CHCl}_2$ 、 $\text{CH}_2\text{FCF}_2\text{CCl}_2\text{F}$ 、
 $\text{CF}_3\text{CF}_2\text{CH}_2\text{Cl}$ 、 $\text{CCl}_2\text{F}_2\text{CF}_2\text{CH}_2\text{F}$ 、
 $\text{CH}_2\text{ClCF}_2\text{CHCl}_2\text{F}$ 、
 $\text{CH}_2\text{FCF}_2\text{CHCl}_2$ 、 $\text{CH}_2\text{FCF}_2\text{CHCl}_2\text{F}$ 、
 $\text{CCl}_2\text{F}_2\text{CF}_2\text{CH}_3$ 、 $\text{CH}_2\text{FCF}_2\text{CH}_2\text{Cl}$ 、
 $\text{CH}_3\text{CF}_2\text{CHCl}_2\text{F}$ の群から選ばれる少なくとも
も1種以上と界面活性剤類とからなる弗素化炭化

水素系混合溶剤組成物。

3. 発明の詳細な説明

〔産業上の利用分野〕

本発明は、代替フロンとして使用できると共に、
溶剤等として優れた特性を有する新規な弗素化炭
化水素系混合溶剤組成物に関するものである。

〔従来の技術〕

弗素化炭化水素系化合物(以下単にフロンとい
う)は、毒性が少なく不燃で化学的に安定なもの
が多く、標準沸点の異なる各種フロンが入手でき
ることから、これらの特性を生かして精密機器類
の脱脂、プリント基板のワックス除去等のための
洗浄剤及び付着水除去用溶剤として1,1,2-トリク
ロロ-1,2,2-トリフルオロエタン(R113)が、
発泡剤としてトリクロロモノフルオロメタン(R
11)が、プロペラントや冷媒としてジクロロジ
フルオロメタン(R12)が使われている。

〔発明が解決しようとする課題〕

化学的に特に安定なR11、R12、R113
は対流圏内での寿命が長く、拡散して成層圏に達

し、ここで太陽光線により分解して発生する塩素ラジカルがオゾンと連鎖反応を起こし、オゾン層を破壊することから、これらの従来のフロンの使用を規制する動きがある。このため、これらの従来のフロンの代わりに、オゾン層を破壊しにくい代替フロンの探策が活発に行われている。本発明は、従来のフロンの使用量を低減し、且つ該フロンが有している優れた特性を満足しながら代替フロンとして使用できる新規なフロン混合物を提供することを目的とするものである。

〔課題を解決するための手段〕

本発明は

CClF₂CF₂CHCl₂ (R224ca)、
CCl₂FCF₂CHClF (R224cb)、
CF₃CF₂CHCl₂ (R225ca)、
CClF₂CF₂CHClF (R225cb)、
CClF₂CF₂CH₂Cl (R234cc)、
CHF₂CF₂CHClF (R235ca)、
CH₃CF₂CCl₂F (R243cc)、
CHF₂CF₂CH₂Cl (R244ca)、

CH₂ClCF₂CH₂Cl (R252ca)、
CHCl₂CF₂CH₃ (R252cb)、
CH₃CF₂CH₂Cl (R262ca)、
CHF₂CF₂CCl₂F (R225cc)、
CHClFCF₂CHClF (R234ca)、
CHF₂CF₂CHCl₂ (R234cb)、
CH₂FCF₂CCl₂F (R234cd)、
CF₃CF₂CH₂Cl (R235cb)、
CClF₂CF₂CH₂F (R235cc)、
CH₂ClCF₂CHClF (R243ca)、
CH₂FCF₂CHCl₂ (R243cb)、
CH₂FCF₂CHClF (R244cb)、
CClF₂CF₂CH₃ (R244cc)、
CH₂FCF₂CH₂Cl (R253ca)、
及びCH₃CF₂CHClF (R253cb)

の群から選ばれる少なくとも1種と界面活性剤とからなる弗素化炭化水素系混合溶剤組成物に関するものである。

本発明の組成物は不燃性又は難燃性であり、且つ従来のフロン類と同等以上の付着水除去効果を

有するものである。

本発明の混合溶剤組成物における界面活性剤の混合割合は0.1～5重量%、好ましくは0.2～2重量%である。

本発明の溶剤組成物に用いられる界面活性剤として好ましいものは、ポリオキシエチレンアルキルエーテル、ポリオキシエチレンポリオキシプロピレンアルキルエーテル、ポリオキシエチレンアルキルエステル、ポリオキシエチレンポリオキシプロピレンアルキルエステル、ポリオキシエチレンアルキルフェノール、ポリオキシエチレンポリオキシプロピレンアルキルフェノール、ポリオキシエチレンソルビタンエステル、ポリオキシエチレンポリオキシプロピレンソルビタンエステル、カプリル酸カプリルアミン、ポリオキシエチレンアルキルアミドである。

本発明の弗素化炭化水素系混合溶剤組成物は、従来の各種用途に使用出来、特に従来のフロン系溶剤よりも付着水の除去作用が優れている点で有利である。

本発明の混合溶剤組成物の具体的な用途としては水洗後の水切り乾燥剤として、特に精密機器、プリント基板、光学レンズ等の付着水除去を挙げることができる。付着水除去方法としては、浸漬、スプレー、超音波洗浄、蒸気洗浄等を採用すればよい。

〔実施例〕

第1表～第4表に示す本発明の混合溶剤組成物を用いて付着水の除去試験を行った。本試験に於けるポリオキシエチレンポリオキシプロピレンアルキルエーテルは分子量1600のものを用いた。30mm×18mm×1.5mm厚のガラス板を純水に浸漬後、本発明の溶剤組成物に20秒間浸して水切りを行い、取り出したガラス板を無水メタノール中に浸漬してその水分増加量から付着水の除去効果を調べた。比較例としてR113についても同様の試験を行った。付着水除去の度合を第1表～第4表に示す。

第 1 表

	混合溶剤組成物	*
実施例 1	R224ca(99.5)/ α -リオキシエチレン α -リ オキシ γ -ロビレンアルキルエーテル(0.5)	◎
2	R224cb()/ "	◎
3	R225ca()/ "	◎
4	R225cb()/ "	◎
5	R234cc()/ "	◎
6	R235ca()/ "	◎
7	R243cc()/ "	◎
8	R244ca()/ "	◎
9	R252ca()/ "	◎
10	R252cb()/ "	◎
11	R262ca()/ "	◎
12	R252cc()/ "	◎
13	R234ca()/ "	◎
14	R234cb()/ "	◎
15	R234cd()/ "	◎

() 内は混合比 [重量%]

* 付着水除去効果

第 2 表

	混合溶剤組成物	*
実施例 16	R235cb(99.5)/ α -リオキシエチレン α -リ オキシ γ -ロビレンアルキルエーテル(0.5)	◎
17	R235cc()/ "	◎
18	R243ca()/ "	◎
19	R243cb()/ "	◎
20	R244cb()/ "	◎
21	R244cc()/ "	◎
22	R253ca()/ "	◎
23	R253cb()/ "	◎

() 内は混合比 [重量%]

* 付着水除去効果

第 3 表

	混合溶剤組成物	*
実施例 1	R224ca(99.5)/カブリン酸 カブリンアミン(0.5)	◎
2	R224cb()/ "	◎
3	R225ca()/ "	◎
4	R225cb()/ "	◎
5	R234cc()/ "	◎
6	R235ca()/ "	◎
7	R243cc()/ "	◎
8	R244ca()/ "	◎
9	R252ca()/ "	◎
10	R252cb()/ "	◎
11	R262ca()/ "	◎
12	R252cc()/ "	◎
13	R234ca()/ "	◎
14	R234cb()/ "	◎
15	R234cd()/ "	◎

() 内は混合比 [重量%]

* 付着水除去効果

第 4 表

	混合溶剤組成物	*
実施例 16	R235cb(99.5)/カブリン酸 カブリンアミン(0.5)	◎
17	R235cc()/ "	◎
18	R243ca()/ "	◎
19	R243cb()/ "	◎
20	R244cb()/ "	◎
21	R244cc()/ "	◎
22	R253ca()/ "	◎
23	R253cb()/ "	◎
比較例	R113(99.5)/ α -リオキシエチレン α -リ オキシ γ -ロビレンアルキルエーテル(0.5)	○

() 内は混合比 [重量%]

* 付着水除去効果

◎; 良好に除去できる。 ○; ほぼ良好。
△; 微量残存。 ×; かなり残存。

【発明の効果】

本発明の弗素化炭化水素混合溶剤組成物は実施例から明らかなように、付着水除去効果の優れたものである。又、従来使用されていたR113と同様に適度な溶解力を持つことから、金属、プラスチック等から成る複合部品に悪影響を与えることなく付着水の除去を行うことができる。

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CLEANUP METHOD FOR OPTICS IN IMMERSION LITHOGRAPHY

5 CROSS-REFERENCE TO RELATED APPLICATION

This application claims priority to U.S. Provisionary Patent Application No. 60/462,556 filed April 11, 2003 and to U.S. Provisionary Patent Application No. 60/482,913 filed June 27, 2003, which are hereby incorporated by reference in their entirety.

10

BACKGROUND OF THE INVENTION

This invention relates to an immersion lithography system and more particularly to methods, as well as systems, for cleaning up the optical element that contacts and absorbs water in the process of immersion lithography.

15 Immersion lithography systems, such as disclosed in WO99/49504 which is herein incorporated by reference for describing the general background of the technology as well as some general considerations related thereto, are adapted to supply a liquid into the space between a workpiece such as a wafer and the last-stage optical element of an optical system for projecting the image of a reticle on the
20 workpiece. The liquid thus supplied improves the performance of the optical system and the quality of the exposure.

The liquid to be supplied may be water for light with wavelength of 193nm although different liquids may be necessary for light with other wavelengths. Because the last-stage optical element of the optical system is exposed to the liquid,
25 there is a possibility that some of the liquid may be absorbed. This possibility is particularly high if the last-stage optical element of the optical system is a lens because calcium fluoride is a common lens material for lithography systems while it is a hygroscopic material, ready to absorb water from the surrounding environment.

The absorbed water may cause several problems. Firstly, it may degrade the
30 image projected by the lens by changing the refractive properties of the lens or by causing the lens to swell to thereby change the geometry of the lens. Secondly, it may cause long-term degradation of the lens due to chemical effects.

Conventional air-immersion exposure lithography systems require the optical elements to be made detachable for maintenance work such as when they are cleaned.

It is a cumbersome and time-consuming operation, however, to remove an optical element and to reset it after it is cleaned or to exchange an optical element for a new one.

It is therefore an object of this invention to provide systems and methods for periodically removing the water from the lens such that the amount of absorbed water will not reach a critical level and the degradation of the image and the long-term damage to the lens can be prevented.

It is another object of the invention to provide systems and methods for making the maintenance of the optical element of an immersion lithography apparatus easier and thereby improving the useful lifetime of the optical element.

SUMMARY OF THE INVENTION

Immersion lithography apparatus of this invention includes a reticle stage arranged to retain a reticle, a working stage arranged to retain a workpiece, an optical system including an illumination source and an optical element opposite the workpiece for having an image pattern of the reticle projected thereon by radiation from the illumination source while defining a gap between the optical element and the workpiece and a fluid-supplying device for providing an immersion liquid between and contacting both the optical element and the workpiece during an immersion lithography process. The apparatus also includes a cleaning device to clean the optical element. Throughout herein, the term "cleaning" will be used to mean both removing immersion liquid that has been absorbed into the optical element and removing dirt, debris, salts and the like.

Many different kinds of the aforementioned cleaning device may be used within the scope of this invention. For example, it may comprise a cleaning liquid having affinity to the immersion liquid to be contacted with the optical element. If the immersion liquid is water, ethanol may serve as the cleaning liquid. As another example, the cleaning device may include a heat-generating device for heating the optical element and/or a vacuum device for generating a vacuum condition on the optical element.

Ultrasonic vibrations may be used for removing the absorbed liquid. An ultrasonic vibrator such as a piezoelectric transducer may be attached to the housing

for the optical element or placed opposite the optical element such that the vibrations may be transmitted to the optical element through a liquid maintained in the gap.

Alternatively, cavitating bubbles may be used for the removal of the absorbed liquid. A pad with fins may be used to generate cavitating bubbles in a liquid
5 maintained in the gap between the pad and the optical element.

According to still another embodiment of the invention, the nozzles through which the immersion liquid is supplied into the gap between the workpiece and the optical element may be used to alternatively supply a cleaning liquid by providing a flow route-switching device such as a switch valve.

10 With a system and method of this invention, the cleaning procedure becomes significantly easier and faster because there is no need to detach the optical element to be cleaned and the cleaning process improves the useful lifetime of the optical element.

15 BRIEF DESCRIPTION OF THE DRAWING

The invention, together with further objects and advantages thereof, may best be understood by reference to the following description taken in conjunction with the accompanying drawings in which:

Fig. 1 is a schematic cross-sectional view of an immersion lithography
20 apparatus on which methods and systems of this invention may be applied;

Fig. 2 is a process flow diagram illustrating an exemplary process by which semiconductor devices are fabricated using the apparatus shown in Fig. 1 according to the present invention;

Fig. 3 is a flowchart of the wafer processing step shown in Fig. 2 in the case of
25 fabricating semiconductor devices according to the present invention;

Fig. 4 is a schematic drawing showing a side view of a portion of the immersion lithography apparatus of Fig. 1;

Fig. 5 is a schematic side view of a portion of another immersion lithography apparatus having an ultrasonic transducer attached so as to serve as its cleaning device;

Fig. 6 is a schematic side view of a portion of still another immersion lithography apparatus having a piezoelectric cleaning device below its optical system;

Fig. 7 is a schematic diagonal view of an example of piezoelectric device;

Fig. 8 is a schematic side view of a portion of still another immersion lithography apparatus having two mutually attached piezoelectric planar members as the cleaning device;

Fig. 9 is a schematic side view of a portion of still another immersion lithography apparatus having a bubble-generating pad as the cleaning device; and

Fig. 10 is a schematic side view of a portion of still another immersion lithography apparatus having a switching device incorporated in the fluid-supplying device.

Throughout herein, components that are similar or equivalent may be indicated by a same symbol or numeral in different figures and may not be explained repetitiously for the simplicity of description.

DETAILED DESCRIPTION OF SPECIFIC EMBODIMENTS

Fig. 1 shows an immersion lithography apparatus 100 on which cleaning methods and systems of this invention may be applied.

As shown in Fig. 1, the immersion lithography apparatus 100 comprises an illuminator optical unit 1 including a light source such as an excimer laser unit, an optical integrator (or homogenizer) and a lens and serving to emit pulsed ultraviolet light IL with wavelength 248nm to be made incidence to a pattern on a reticle R. The pattern on the reticle R is projected on a wafer W coated with a photoresist at a specified magnification (such as 1/4 or 1/5) through a telecentric light projection unit PL. The pulsed light IL may alternatively be ArF excimer laser light with wavelength 193nm, F₂ laser light with wavelength 157nm or the i-line of a mercury lamp with wavelength 365nm. In what follows, the coordinate system with X-, Y- and Z-axes as shown in Fig. 1 is referenced to explain the directions in describing the structure and functions of the lithography apparatus 100. For the convenience of disclosure and

description, the light projection unit PL is illustrated in Fig. 1 only by way of its last-stage optical element (such as a lens) 4 disposed opposite to the wafer W and a cylindrical housing 3 containing the rest of its components.

5 The reticle R is supported on a reticle stage RST incorporating a mechanism for moving the reticle R in the X-direction, the Y-direction and the rotary direction around the Z-axis. The two-dimensional position and orientation of the reticle R on the reticle stage RST are detected by a laser interferometer (not shown) in real time and the positioning of the reticle R is effected by a main control unit 14 on the basis of the detection thus made.

10 The wafer W is held by a wafer holder (not shown) on a Z-stage 9 for controlling the focusing position (along the Z-axis) and the tilting angle of the wafer W. The Z-stage 9 is affixed to an XY-stage 10 adapted to move in the XY-plane substantially parallel to the image-forming surface of the light projection unit PL. The XY-stage 10 is set on a base 11. Thus, the Z-stage 9 serves to match the wafer
 15 surface with the image surface of the light projection unit PL by adjusting the focusing position (along the Z-axis) and the tilting angle of the wafer W by the auto-focusing and auto-leveling method, and the XY-stage 10 serves to adjust the position of the wafer W in the X-direction and the Y-direction.

The two-dimensional position and orientation of the Z-stage 9 (and hence also
 20 of the wafer W) are monitored in real time by another laser interferometer 13 with reference to a mobile mirror 12 affixed to the Z-stage 9. Control data based on the results of this monitoring are transmitted from the main control unit 14 to a stage-driving unit 15 adapted to control the motions of the Z-stage 9 and the XY-stage 10 according to the received control data. At the time of an exposure, the projection light
 25 is made to sequentially move from one to another of different exposure positions on the wafer W according to the pattern on the reticle R in a step-and-repeat routine or in a step-and-scan routine.

The lithography apparatus 100 being described with reference to Fig. 1 is an
 30 immersion lithography apparatus and is hence adapted to have a liquid (or the "immersion liquid") 7 of a specified kind such as water filling the space (the "gap") between the surface of the wafer W and the lower surface of the last-stage optical

element 4 of the light projection unit PL at least while the pattern image of the reticle R is being projected on the wafer W.

The last-stage optical element 4 of the light projection unit PL may be detachably affixed to the cylindrical housing 3 and is designed such that the liquid 7 will contact only the last-stage optical element 4 and not the cylindrical housing 3 because the housing 3 typically comprises a metallic material and is likely to become corroded.

arr 1
10 The liquid 7 is supplied from a liquid supply unit 5 that may comprise a tank, a pressure pump and a temperature regulator (not individually shown) to the space above the wafer W under a temperature-regulated condition and is collected by a liquid recovery unit 6. The temperature of the liquid 7 is regulated to be approximately the same as the temperature inside the chamber in which the lithography apparatus 100 itself is disposed. Numeral 21 indicates supply nozzles through which the liquid 7 is supplied from the supply unit 5. Numeral 23 indicates
15 recovery nozzles through which the liquid 7 is collected into the recovery unit 6. It is to be reminded, however, that the structure described above with reference to Fig. 1 is not intended to limit the scope of the immersion lithography apparatus to which the cleaning methods and devices of the present invention are applicable. In other words, it goes without saying that the cleaning methods and devices of the present invention
20 are applicable to immersion lithography apparatus of many different kinds. In particular, it is to be reminded that the numbers and arrangements of the supply and recovery nozzles 21 and 23 around the light projection unit PL may be designed in a variety of ways for establishing a smooth flow and quick recovery of the immersion liquid 7.

25 A method embodying this invention of removing the portion of the liquid 7 such as water absorbed by the last-stage optical element 4 made of a hygroscopic material, as well as dirt, debris, etc., is explained next with reference to Figs. 1 and 4. After the wafer W is exposed with light from the illuminator optical unit 1 through the light projection unit PL in the presence of the liquid 7 as shown in Fig. 1, the liquid 7
30 is removed from underneath the light projection unit PL and a cleaning device 30 is brought into contact with the last-stage optical element 4 as shown in Fig. 4. In the case of a portable kind, as shown in Fig. 4, the cleaning device 30 may be placed on

the Z-stage 9 or the aforementioned wafer holder thereon, as shown in Fig. 4, in place of the wafer W.

Different types and kinds of cleaning device 30 can be used for the purpose of this invention. As a first example, the cleaning device 30 may be a container
5 containing a liquid ("cleaning liquid") with a strong affinity to the immersion liquid 7 which is absorbed by the optical element 4. If the immersion liquid 7 is water, the cleaning device 30 may contain ethanol since ethanol has a strong affinity to water. Any cleaning liquid may be used provided it has a sufficiently strong affinity to the liquid to be removed and does not damage the optical element 4 or its coating. The
10 bottom surface of the optical element 4 is soaked in the cleaning liquid for a period of time sufficiently long to reduce the level of the absorbed liquid. The cleaning device 30 is removed thereafter and the optical element 4 is ready to be exposed to the liquid 7 again.

As another example, the cleaning device 30 may contain a heat-generating
15 device and/or a vacuum device (not separately shown). The combination of heat and vacuum on the surface of the optical element 4 causes the absorbed liquid to undergo a phase change into vapor, or to evaporate from the surface. The reduction in liquid density on the surface of the optical element 4 draws the liquid 7 that is absorbed more deeply in the element 4 to the surface.

20 Fig. 5 shows a third example wherein use is made of an ultrasonic transducer (or ultrasonic vibrator) 32 attached to the housing 3 of the light projection unit PL. As the ultrasonic transducer 32 (such as a piezoelectric transducer) is activated, pressure waves are generated and propagated, serving to clean the surface of the optical element 4.

25 During the cleaning operation in Fig. 5, the gap adjacent the optical element 4 is filled with the immersion liquid 7. In this case, the supply and recovery nozzles can continue to supply and collect the immersion liquid 7, or the supply and recovery nozzles can stop supplying and collecting the immersion liquid 7. Also during the cleaning operation, the optical element 4 can face a surface of wafer W, a surface of
30 the Z-stage 9, or a surface of another assembly.

Fig. 6 is a fourth example using a vibratory tool 34 placed below the optical element 4 to be cleaned. The tool 34 may be shaped like the wafer W with thickness more or less equal to that of the wafer W, or about 0.5-1mm, and may be made

entirely of a piezoelectric material such that its thickness will fluctuate when activated. As the tool 34 is placed below the optical element 4, like the wafer W as shown in Fig. 1, and the gap between the optical element 4 and the tool 34 is filled with the liquid 7, pressure waves are generated in the immersion liquid 7 to clean the optical element.

During the cleaning operation of Fig. 6, the gap adjacent the optical element 4 is filled with the immersion 7. In this case, the supply and recovery nozzles can continue to supply and collect the immersion liquid, or the supply and recovery nozzles can stop supplying and collecting the immersion liquid 7. In other example, the vibrator tool 34 may be a ultrasonic transducer attached to the wafer holder on a Z-stage 9, or another assembly.

Fig. 7 shows another tool 36, structured alternatively, having a plurality of piezoelectric transducers 38 supported by a planar supporting member 39.

Fig. 8 shows still another example of a cleaning device having two planar members 40 of a piezoelectric material attached in a face-to-face relationship and adapted to oscillate parallel to each other and out of phase by 180° with respect to each other. As a result, these members 40, attached to each other, will vibrate in the transverse directions, as shown in Fig. 8 in a very exaggerated manner. The vibration has node points at constant intervals where the members 40 are not displaced. The members 40 are supported at these node points on a supporting member 41. As voltages are applied to these members 40 so as to cause the vibrations in the mode described above, ultrasonic pressure waves are thereby generated and propagated through the liquid 7, and the optical element 4 is cleaned, as desired.

Fig. 9 shows still another example of a liquid removal system characterized as cleaning the optical element 4 by creating cavitating bubbles. Cavitating bubbles trapped and energized by ultrasound are high-temperature, high-pressure microreactors and intense energy released by the implosive compression of the bubbles is believed to rip molecules apart. The example shown in Fig. 9 is characterized as comprising a pad 43 with fins protruding upwards and rapidly moved horizontally as shown by an arrow below the optical element 4 with a bubble-generating liquid 17 filling the gap in between (means for moving the pad 43 not being shown). As the pad 43 is thus moved, the fins serve to stir the liquid 17 and to generate cavitating bubbles which in turn serve to clean the optical element.

Fig. 10 shows a different approach to the problem of cleaning the last-stage optical element 4 by applying a cleaning liquid on its bottom surface by using the same source nozzles 21 used for supplying the immersion liquid 7. For this purpose, a switch valve 25 is inserted between the supply nozzle 21 and the liquid unit 5 such that the immersion liquid 7 and the cleaning liquid can be supplied selectively through the supply nozzle 21.

It is again to be reminded that the cleaning methods and systems according to this invention are applicable to immersion lithography apparatus of different kinds and types, say, having different numbers of source nozzles. A switch valve as described above need not necessarily be provided to each of the source nozzles but may be provided to a group of the source nozzles.

It may be the wafer W itself or a pad 18 of a suitable kind that may be placed below the optical element 4 to provide a suitable gap in between when the cleaning liquid is thus supplied through the supply nozzles 21. This embodiment of the invention is advantageous because the same nozzles already present for supplying the immersion liquid can be utilized for the cleaning process.

Although various methods have been separately described above, it goes without saying that they may be used in combinations although not separately illustrated in drawings. For example, the pad 43 with fins shown in Fig. 9 may be used instead of the pad 18 of Fig. 10. In other words, the examples described above are not intended to limit the scope of the invention and many modifications and variations are possible within the scope of this invention. For example, a polishing pad similar to one used in chemical mechanical polishing may be used for this purpose. The cleanup procedure shown in Figs. 4-10 may be carried out with ultraviolet light. The light may irradiate the optical element 4. The light may be normal exposure light from the illuminator optical unit 1 or some other light of an appropriate wavelength for the purpose of the cleanup. In other example, the ultraviolet light for the purpose of the cleanup may be used without the cleanup procedure shown in Figs. 4-10, and may be used under a condition in which the gap adjacent the optical element 4 is filled with the immersion liquid 7 from the liquid supply unit 5. All such modifications and variations that may be apparent to a person skilled in the art are intended to be within the scope of this invention.

Again, it should be noted that any of the above described cleaning methods for removing immersion fluid absorbed by the last-stage optical element as well as salts, deposits, dirt and debris that may have accumulated. The term cleaning therefore refers to both of these phenomena herein.

5 Fig. 2 is referenced next to describe a process for fabricating a semiconductor device by using an immersion lithography apparatus incorporating a liquid jet and recovery system embodying this invention. In step 301 the device's function and performance characteristics are designed. Next, in step 302, a mask (reticle) having a pattern is designed according to the previous designing step, and in a parallel step
10 303, a wafer is made from a silicon material. The mask pattern designed in step 302 is exposed onto the wafer from step 303 in step 304 by a photolithography system such as the systems described above. In step 305 the semiconductor device is assembled (including the dicing process, bonding process and packaging process), then finally the device is inspected in step 306.

15 Fig. 3 illustrates a detailed flowchart example of the above-mentioned step 304 in the case of fabricating semiconductor devices. In step 311 (oxidation step), the wafer surface is oxidized. In step 312 (CVD step), an insulation film is formed on the wafer surface. In step 313 (electrode formation step), electrodes are formed on the wafer by vapor deposition. In step 314 (ion implantation step), ions are implanted in
20 the wafer. The aforementioned steps 311-314 form the preprocessing steps for wafers during wafer processing, and selection is made at each step according to processing requirements.

At each stage of wafer processing, when the above-mentioned preprocessing steps have been completed, the following post-processing steps are implemented.
25 During post-processing, initially, in step 315 (photoresist formation step), photoresist is applied to a wafer. Next, in step 316, (exposure-step), the above-mentioned exposure device is used to transfer the circuit pattern of a mask (reticle) to a wafer. Then, in step 317 (developing step), the exposed wafer is developed, and in step 318 (etching step), parts other than residual photoresist (exposed material surface) are
30 removed by etching. In step 319 (photoresist removal step), unnecessary photoresist remaining after etching is removed. Multiple circuit patterns are formed by repetition of these preprocessing and post-processing steps.

While a lithography system of this invention has been described in terms of several preferred embodiments, there are alterations, permutations, and various substitute equivalents which fall within the scope of this invention. It should also be noted that there are many alternative ways of implementing the methods and

5 apparatuses of the present invention. It is therefore intended that the following appended claims be interpreted as including all such alterations, permutations, and various substitute equivalents as fall within the true spirit and scope of the present invention.

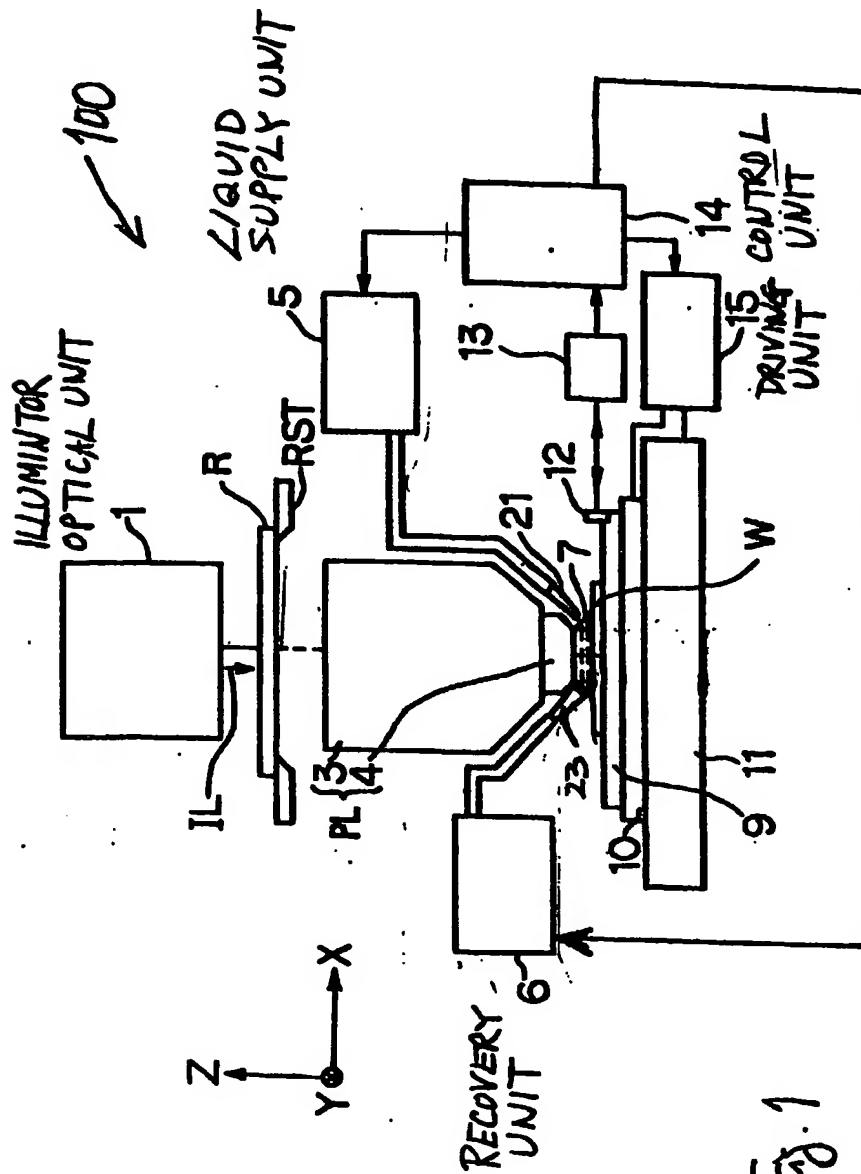


Fig. 1

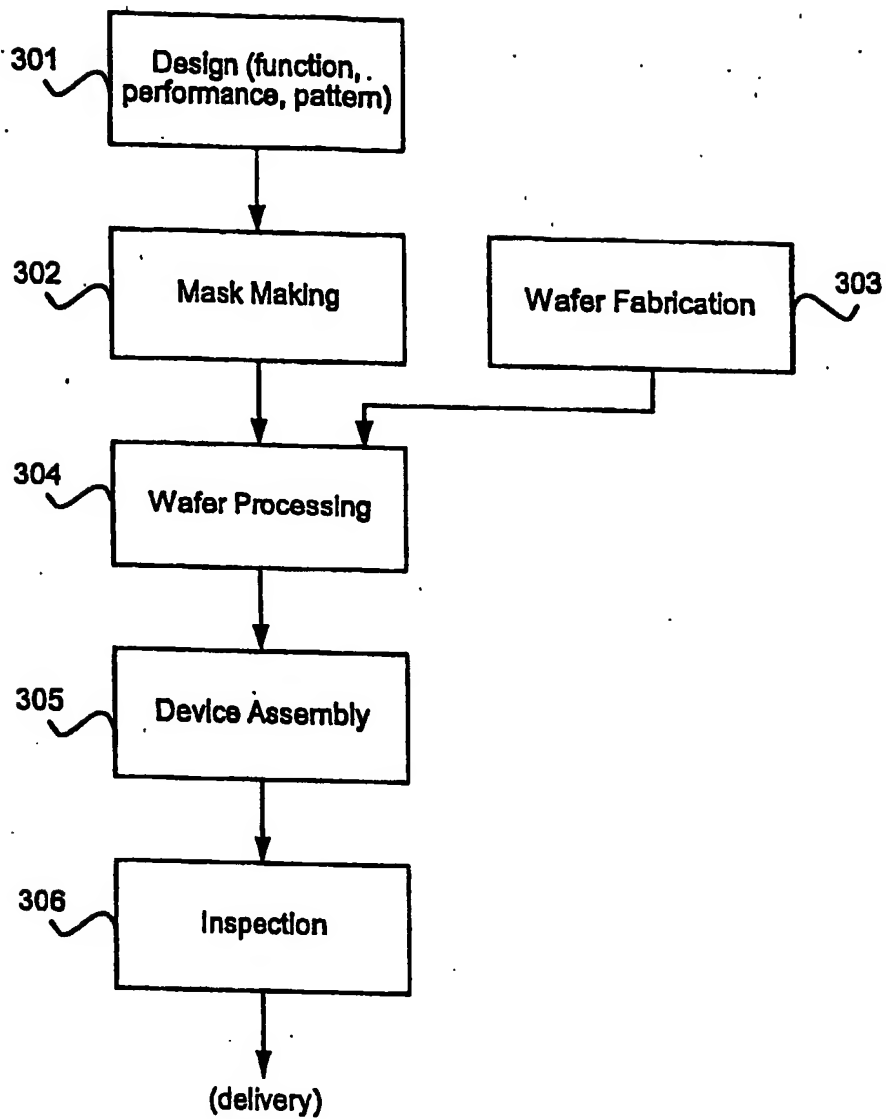


Fig. 2

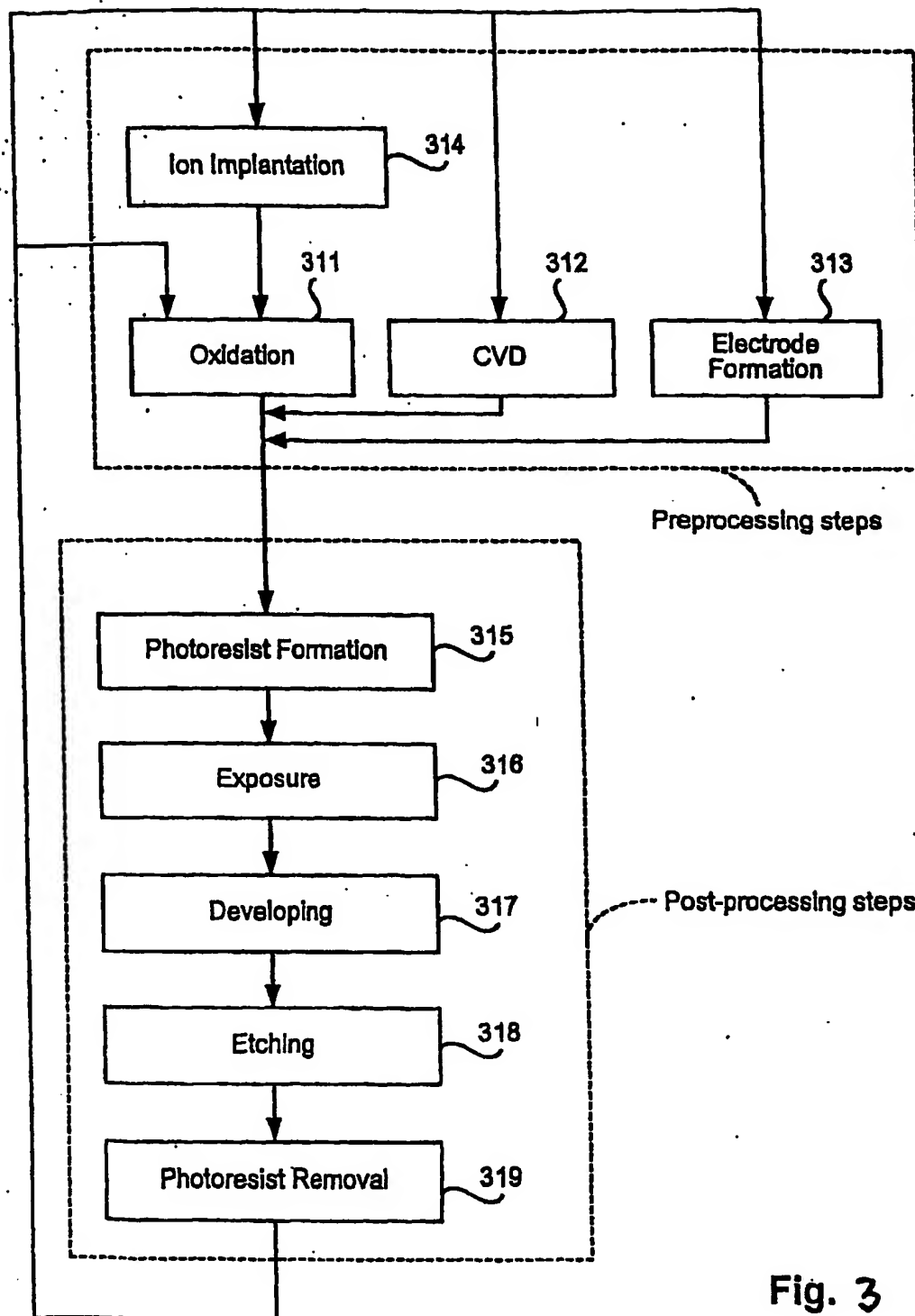
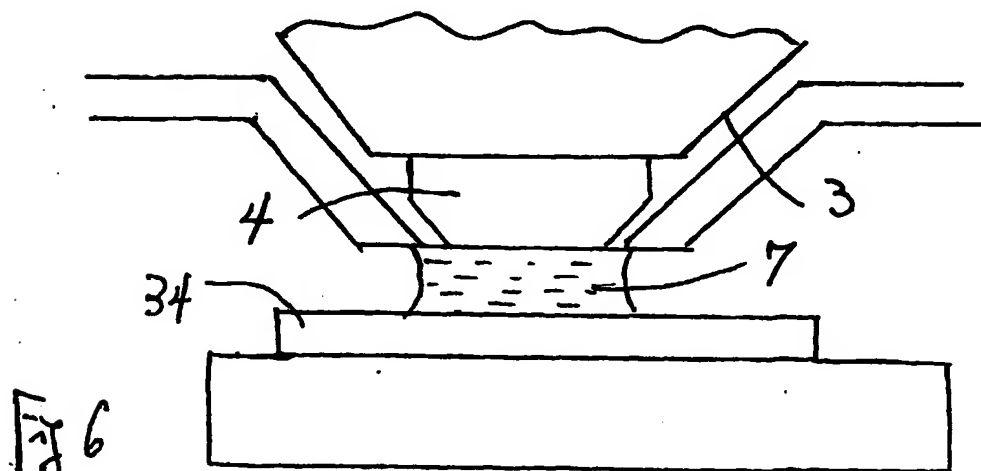
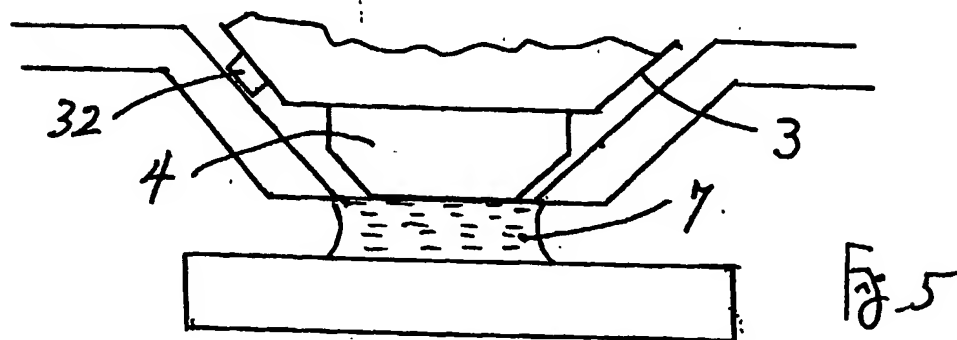
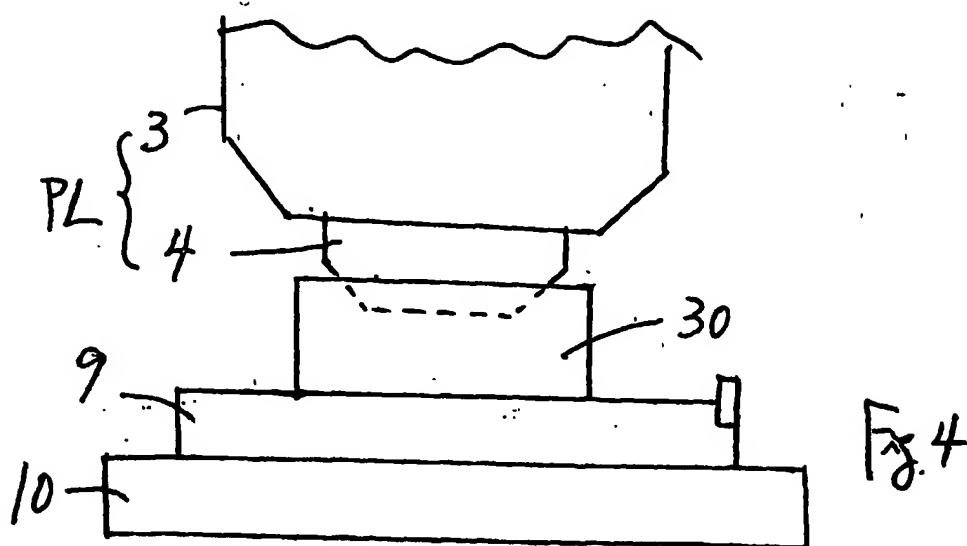


Fig. 3



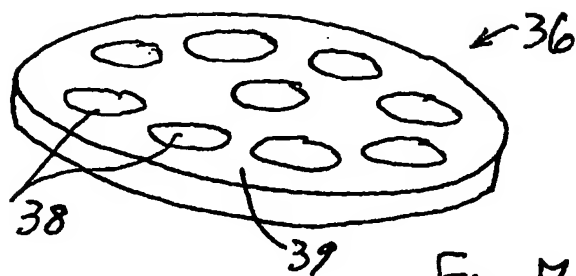


Fig. 7

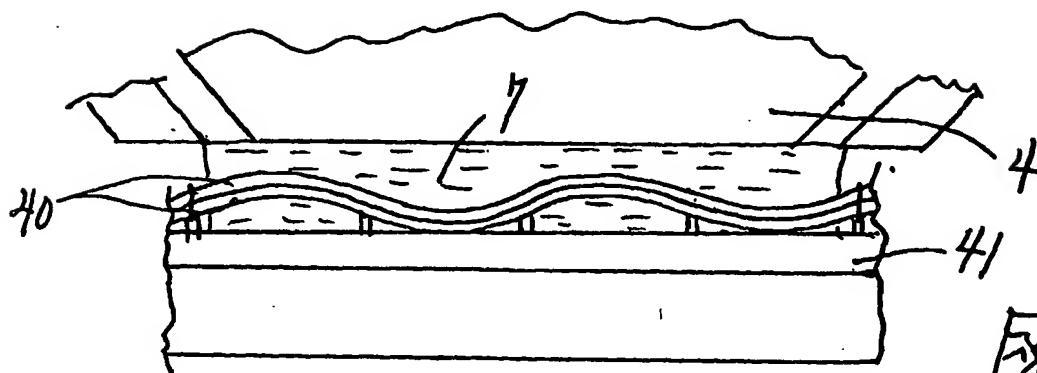


Fig. 8

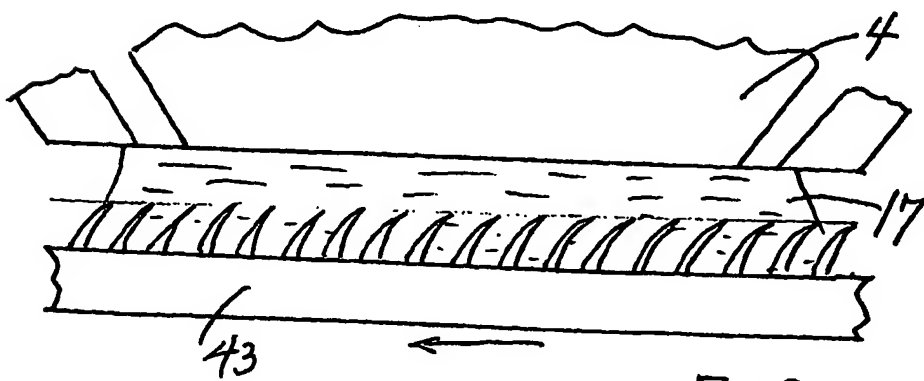


Fig. 9

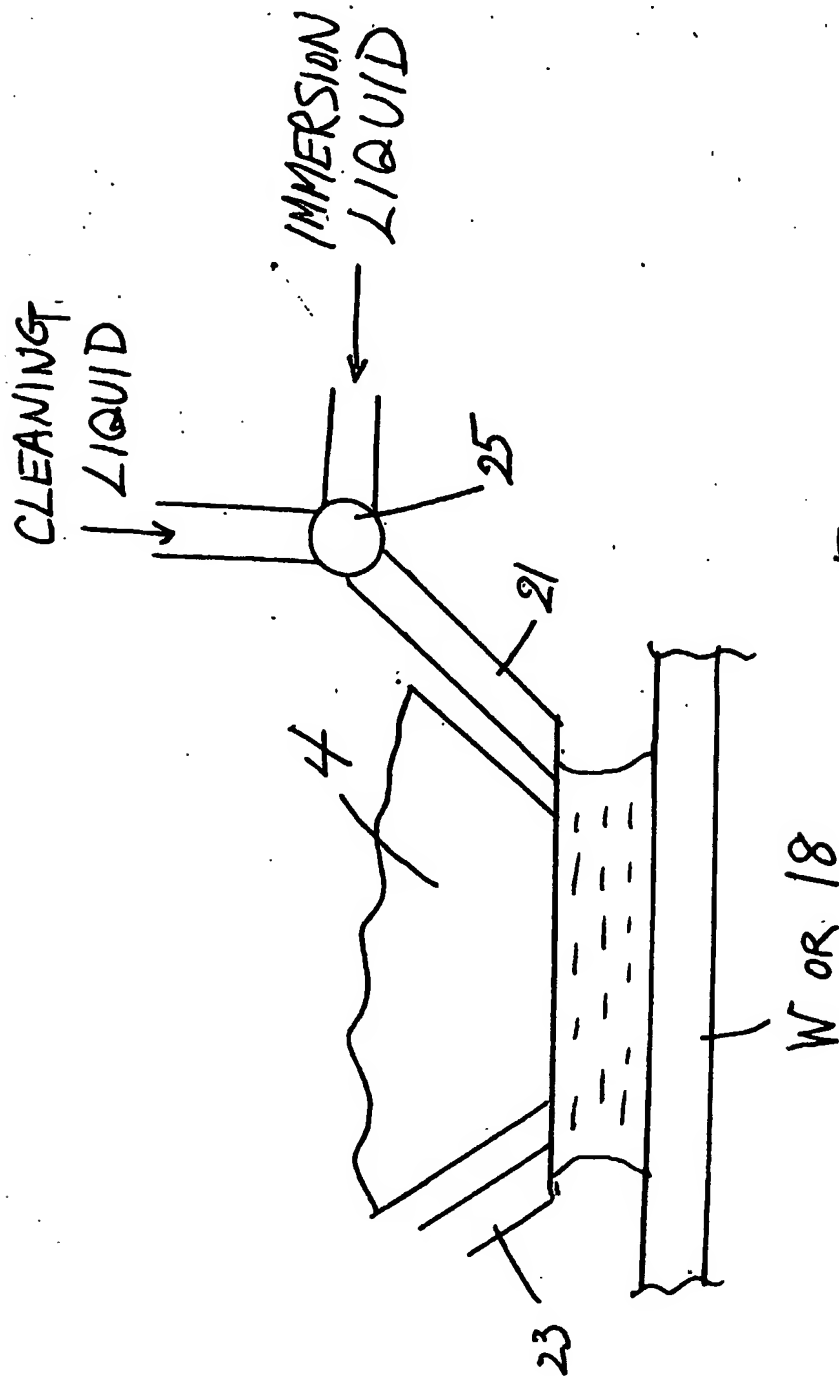


Fig. 10

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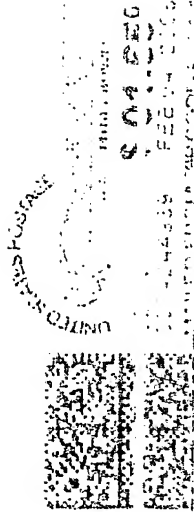
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